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## (54) IMPROVEMENTS IN OR RELATING TO SEMICONDUCTOR LAYERS

(71) We, SIEMENS AKTIENGESELLSCHAFT, a German Company, of Berlin and Munich, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to the production of epitaxially deposited layers of semiconductor material on a substrate, wherein, in a first step, a seed layer consisting of the semiconductor material is deposited on the substrate by a thermal, irreversible decomposition of a compound of the semiconductor material, and wherein, in a second step, further semiconductor material is then deposited on this seed layer.

Processes for the production of epitaxially deposited layers of semiconductor material on a substrate are already known. Such a process is described, for example, in German Patent Specification No. 1,619,980 as open to public inspection. In this process, a seed layer consisting of the semiconductor material to be deposited is formed on the substrate in a first processing step in which silane is thermally decomposed, for example, from a gas consisting of silane and hydrogen. Subsequently, in a second step, further semiconductor material is deposited on this seed layer by the thermal decomposition of a halide of the semiconductor material.

It is an object of the present invention to provide an improved form of the above described process for the production of epitaxially deposited layers of semiconductor material on a substrate.

According to the invention, there is provided a process for the production of an epitaxially deposited semiconductor layer on a substrate comprising, in a first step, depositing a seed layer of a semiconductor material on a substrate by the thermal irreversible decomposition of a reaction gas consisting of or containing a gaseous compound of the semiconductor material but free from hydrogen halide, and thereafter, in a second

step, depositing further semiconductor material on said seed layer at the same temperature as used in the first step from the same reaction gas to which a hydrogen halide has been added.

In this process, in the second process step for the further deposition of semiconductor material on the seed layer, one does not, as in the known processes referred to above, use a halide of the semiconductor material. Instead, one merely adds hydrogen halide to the gas employed, in the first processing step which serves for the deposition of the seed layer, and, in the case of silicon, may consist of or include, for example, silane.

One advantage of the process of the present invention consists in the fact that merely a single gaseous semiconductor compound is required for the deposition of semiconductor material during both the first process step in which the irreversible decomposition and deposition take place, and during the second process step in which the deposition proceeds in accordance with an equilibrium reaction. Thus, there is a continuous transition from the first to the second process step, for which reason, a more homogeneous crystal structure can be achieved for the epitaxially deposited semiconductor layer than in the case of the known processes.

In contrast to the high growth rate during the formation of the seed layer, there is a lower growth rate during the further deposition of semiconductor material on the seed layer. The growth rate can advantageously be controlled by a controlled addition of hydrogen halide to a preferably constant supply of the reaction gas including the compound to be decomposed (for example, silane) which supply is maintained during both deposition steps. This addition of hydrogen halide influences the chemical equilibrium reactions which take place during the second process step and which lead respectively to the deposition of semiconductor material, and removal of previously deposited material.

With the aid of the equilibrium reactions

which take place in the second processing step, incorrectly or poorly incorporated lattice atoms of the semiconductor layer can be removed and replaced in a better manner by new deposition.

The invention will now be further described with reference to the drawing, in which:—

Figure 1 is a schematic side view of a substrate with a semiconductor layer deposited thereon by a process in accordance with the invention; and

Figure 2 is a graph showing the growth rate of the semiconductor material during the second process step of a process in accordance with the invention, in dependence upon the hydrogen chloride concentration.

Referring to Figure 1, a substrate 1 is preferably made of Mg-Al-spinel or sapphire. Two layers of semiconductor material are applied to the substrate, a seed layer 2 and a subsequent layer 3. The seed layer 2 is deposited on the substrate by the irreversible, thermal decomposition of a reaction gas, preferably consisting of silane and hydrogen. Subsequently, a hydrogen halide, in particular hydrogen chloride or hydrogen bromide, is added to the reaction gas, and the layer 3 is formed as a result of a chemical equilibrium reaction.

The process of the invention is preferably carried out as follows. Substrate wafers, which have previously been cut and polished along specific crystal planes, are firstly freed from the damage layer. This is preferably effected by annealing the substrate wafers at a temperature of more than 1000°C in a hydrogen atmosphere, or by chemically wet-etching the substrate wafers at elevated temperatures, preferably with phosphoric acid at temperatures of between 200° and 400°C. The substrate wafers which have been so treated are now preferably placed in a water-cooled quartz vessel on an inductively heated, high-purity carbon plate. After the vessel has been flushed out with hydrogen or an inert gas, the carbon plate with the substrate wafers arranged thereupon, is then brought to the desired deposition temperature, the hydrogen supply being continued throughout these operations. Preferably, the deposition temperature is above 1000°C when hydrogen is used and below 1000°C (e.g. between 880 and 980°C) when an inert gas, such as helium, is used. By opening a valve, silane is added to the continuous supply of hydrogen or inert gas to produce a mixture of 1 to 3% by volume of silane in the hydrogen or inert gas. Using a quartz vessel with a rectangular cross-section of approximately 20 cm<sup>2</sup> approximately 2000 to 4000 l/h of hydrogen and 500 to 1500 l/h of a mixture of 1% by volume of silane in hydrogen are preferably used to form the reaction gas. The silane supply is main-

tained until there is a continuous seed layer formed on the substrate. Preferably, the silane supply is continued until the seed layer has a thickness of 0.05 to 0.3  $\mu$ . In the second process step which now follows, hydrogen chloride is additionally supplied to the reaction vessel without the silane and hydrogen flow, or the temperature, being altered. For a vessel cross-sectional area of approximately 20 cm<sup>2</sup>, preferably about 5 to 150 l/h hydrogen chloride is supplied. Since, after the addition of the hydrogen chloride, a chemical equilibrium reaction takes place, the growth rate of the layer 3 is less than the growth rate of the seed layer 2.

Figure 2 illustrates the dependence of the growth rate of a growing silicon semiconductor layer with a constant supply of silane and hydrogen, upon the concentration of the added hydrogen chloride gas, when 1100 l/h of a mixture of 1% by volume of silane in hydrogen and in addition 4000 l/h hydrogen is fed to a quartz cell possessing a rectangular cross-section with an area of approximately 20 cm<sup>2</sup>. From this curve, the desired low growth rates may be determined as a function of the hydrogen chloride addition for the second process step.

When the desired layer thickness has been attained, the silane, the hydrogen and the hydrogen chloride supply are all interrupted. The heating of the substrate wafers with the semiconductor material deposited thereon is terminated.

Instead of silicon, germanium may be deposited on the substrate. In this case, the deposition of the seed layer on the substrate is effected by the irreversible thermal decomposition of a gas consisting of GeH<sub>4</sub> and hydrogen at a temperature of 600° to 850°C. The further deposition of germanium preferably takes place at the same temperature, again making use of an equilibrium reaction which occurs after the addition of hydrogen halide.

#### WHAT WE CLAIM IS:—

1. A process for the production of an epitaxially deposited semiconductor layer on a substrate comprising, in a first step, depositing a seed layer of a semiconductor material on a substrate by the thermal irreversible decomposition of a reaction gas consisting of or containing a gaseous compound of the semiconductor material but free from hydrogen halide, and thereafter, in a second step, depositing further semiconductor material on said seed layer at the same temperature as used in the first step from the same reaction gas to which a hydrogen halide has been added.

2. A process as claimed in Claim 1, wherein said substrate is of sapphire.

3. A process as claimed in Claim 1, 130

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wherein said substrate is of a Mg/Al-spinel.

4. A process as claimed in any one of Claims 1 to 3, wherein before said first process step, said substrate is chemically wet-  
5 etched at a temperature of between 200 and 400°C with phosphoric acid.

5. A process as claimed in any one of Claims 1 to 3, wherein before said first process step, said substrate is annealed at a  
10 temperature above 1000°C in a hydrogen atmosphere.

6. A process as claimed in any one of the preceding Claims, wherein said semiconductor material is silicon, and wherein  
15 said seed layer is deposited at a substrate temperature of above 1000°C from a reaction gas consisting of silane and hydrogen.

7. A process as claimed in Claim 6, wherein said reaction gas is produced by  
20 mixing a mixture of 1—3% by volume of silane in hydrogen, with additional hydrogen.

8. A process as claimed in any one of Claims 1 to 5, wherein said semiconductor material is silicon and said seed layer is de-  
25 posited at a substrate temperature of below 1000°C from a reaction gas consisting of silane and an inert gas.

9. A process as claimed in Claim 8, wherein said reaction gas is produced by

mixing a mixture of 1—3% by volume of silane in helium, with additional helium. 30

10. A process as claimed in Claim 8 or Claim 9, wherein said seed layer is deposited at a substrate temperature of between 850  
35 and 980°C.

11. A process as claimed in any one of Claims 1 to 5, wherein said semiconductor material is germanium and wherein said seed layer is deposited at a substrate temperature of 600—850°C, from a reaction gas con-  
40 sisting of GeH<sub>4</sub> and hydrogen.

12. A process for the production of an epitaxially deposited semiconductor layer on a substrate substantially as hereinbefore described with reference to the drawing. 45

13. An epitaxially deposited semiconductor layer produced by a process as claimed in any one of the preceding Claims.

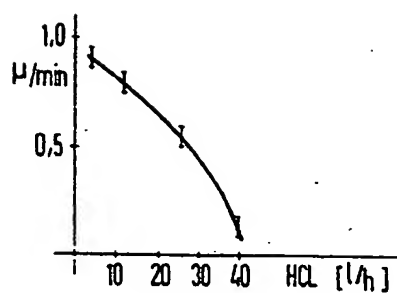
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Fig.1



Fig.2



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